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Study of Compressional and Elastic Behavior of Nano- ZnO Crystal at High Pressure

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ABSTRACT

In the present paper, we have reported the results of a theoretical investigation on the compressional and elastic behavior of ZnO nanocrystal at high pressure during transformation from wurtzite to rock salt structure. A simple theory is proposed to predict the transition pressure (P_T) and bulk modulus of ZnO nanocrystal at high pressure which gets support from the Mie-Gruneisen theory of thermal expansivity as formulated by Born and Huang. We have considered the Tait's equation of state to study the effect of pressure on the phase transition from wurtzite (W) to rock salt (R) phase in zinc oxide nanomaterial. The results obtained are found to present a good agreement with the available experimental data. A good agreement between theoretical and experimental results demonstrates the validity of the equation of state used in the present study to explain the compressional behavior of nanomaterials at high pressure.

Keywords: structural transition; bulk modulus; equation of state.

1. INTRODUCTION

The nanomaterials are expected to be the turning point of the next technological revolution in solid state electronics and to have a considerable impact practically in all domains of science. The nanomaterials are very sensitive to external parameters like pressure and temperature. The study of nanomaterials under high pressure provides a possible path to expand the range of available solid state materials. High Pressure applications have the potential for the exploration of infinity of paths for nano-assembling in a controlled way and constitute a unique root for the elaboration of new materials. The physical properties of nanomaterials depend strongly on the structure and interatomic distances. High Pressure can vary these distances, which

implies that one can study relationship between structure and properties of such materials. Due to the high pressure on nanomaterials, many effects occur, such as (i) modification of interactions between nano-object and pressure transmitting medium, (ii) transformation of nano-constitutive elements, and (iii) transformation of the interactions between nano-object due to drastic change in surface-volume ratio of atoms. This is why the pressure induced studies on nanomaterials have attracted the attention of the researchers working in this field.

Zinc oxide is one of the most important and widely used materials, such as in optoelectronic devices[1]. Its high Pressure behavior is also valuable for geophysical and fundamental material physics. ZnO crystallizes to a hexagonal wurtzite-type (space group $P6_3mc$, B4) structure under ambient conditions, and transforms to a rock salt type (space group Fm3m, B1) structure at high pressure. During past, the extensive studies have been made in many different areas[2-3], including the characterization of properties and structures under high pressures[4]. In contrast to the corresponding bulk counter parts, nanostructured ZnO has enhanced electronic and photo conducting properties. Nanometer scale sample with well-controlled shapes have been successfully fabricated, and they are potentially great candidates for nanodevices, like field effect transistors and gas sensors[5,6]. Recent studies on the neighborhood wurtzite-type, ZnO nanostructures like ZnO–nanowire[7,8], ZnO–nanotube[9], ZnO–nanobelt[10] and ZnO–nanorod[11] showed an unstable behavior under high pressure. The wurtzite (B4) phase transforms to rock salt-type (B1) phase upon compression to some certain threshold pressure. The B4 - to- B1 phase transition in ZnO has been extensively investigated using experimental and theoretical approaches[12-16], but the transition pressure varies in a broad range depending on the morphology of ZnO as well as other experimental conditions. It was well established that the B4 - to - B1 phase Transition for bulk ZnO takes place at 9±0.2 GPa[16,17], however, the transition pressure for ZnO nanocrystal falls in the broad range from 10.5 to 15.1 GPa as the grain size of the nanocrystal varies from 50 to 12 nm[12-16].

In contrast to bulk ZnO and ZnO nanocrystal, which have been extensively studied, only a few high pressure studies have been carried out on 1D ZnO so far. Zhanjun *et al*.[7] reported a high- pressure study on ZnO - nanowires showing that the B4-to-B1 phase transition took place at 5.64 GPa and found that both the volume change (ΔV) and the transition pressure (P_T) of nanowires are lower than that of the bulk ZnO and decreases as the diameter of the nanowires decreases. It is observed that the theoretical value of transition pressure (P_T) obtained by Zhanjun et al. is much smaller than that of 8.3 GPa calculated by Kulkarni *et al*.[18] by using the molecular dynamic theory. Recently, Dong *et al*.[8] have reported the first high pressure study of ZnO–nanowires using the synchrotron X-ray diffraction technique. They compressed the nanomaterial to high pressures up to 26 GPa, followed by decompression and observed that on applying compression on nanowire of width 50-100nm with an average length of 3 to 4 µm, the B4 phase persisted to 12.9 GPa, as indicated by the consistent indexing of all reflections associated with this phase.

The transformation starts from wurtzite to rock salt phase at 13.7 GPa and coexistence of mixed phase remains till 22 GPa. The complete transformation from wurtzite to rock salt phase was observed at 24.1 GPa, as suggested by the disappearance of all diffraction reflections associated with the B4 phase .The theoretical studies performed by the previous workers[7,8] to predict the transition pressure(P_T) in ZnO–nanowire, however ,could not explain the experimental results satisfactorily.

The high pressure behavior of Zinc oxide (ZnO) nanotube and ZnO - nanorods have been studied by Hou *et al*.[19] and Wu *et al*.[11] by using in-situ synchrotron X-ray diffraction and in-situ energy dispersive X-ray diffraction methods respectively during past years. The transformation from the hexagonal wurtzite (B4) to the cubic rock salt (B1) phase has been observed to start at 10.5 GPa and completed at 18.4 GPa[19] in ZnO - nanotubes. But in ZnO - nanorods the transformation from wurtzite structure to rock salt structure starts at 8.0GPa and ended at about 27.0 GPa[15]. This indicates that in such both systems the transformation of phase coexists (wurtzite + rock salt) up to 18.4 GPa in ZnO nanotube and 27.0 GPa in ZnO-nanorods like in ZnO -nanowire in which the transformation is completed at 22.4 GPa. However, in nano- ZnO crystal, the transformation from the hexagonal wurtzite (B4) to the cubic rock salt (B1) phase begins around 10.5 GPa with both phases co-existing upto 13 GPa[12]. From the above observations this can be seen that in ZnO nanostructured materials the structural phase transition does not occur suddenly but the mixed phase of wurtzite and rock salt persists till the transformation to the pure rock salt phase is completed at their respective transition pressures. Several experimental studies have been thus performed to understand the high pressure behavior of nanostructure materials. However, the theoretical efforts are lacking. So, it is legitimate and may be useful to present a appropriate theoretical analysis of experimental studies on the compressional behavior of nanosystems and compare it with experimental data and earlier formulations. The method of analysis of nanostructure materials is given in section 2.The results and discussion are given in section 3.

2. METHOD OF ANALYSIS

Investigation of compressional behavior of bulk solids has been the subject of great interest[21-22] for its importance in understanding the microscopic behavior of bulk materials in physics and geophysics. The usual Tait's equation of state is obtained by assuming the fact that the product of the thermal expansion coefficient (α) and the bulk modulus (B) is constant under the effect of pressure, i.e.

$$\alpha_o B_o = \alpha_T B_T = \text{constant} \tag{1}$$

Differentiation of equation (1) with respect to volume at constant temperature gives

$$\alpha\left(\frac{dB}{dV}\right)_T + B\left(\frac{d\alpha}{dV}\right)_T = 0 \tag{2}$$

Anderson –Gruneisen parameter (δ_T) is defined as

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_T \tag{3}$$

Where δ_T is Anderson-Gruneisen parameter at constant temperature T.

In view of equations (2) and (3), we get

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_T = -\frac{V}{B}\left(\frac{dB}{dV}\right)_T \quad (4)$$

Assuming δ_T to be independent of V,

$$\delta_T = \left(\frac{dB}{dP}\right)_T = B_o' \quad (5)$$

Anderson-Gruneisen parameter δ_T and η = V/Vo (where Vo is the initial volume of the unit cell) are related by the following relation[22],

$$\left(\frac{\delta_T+1}{\eta}\right) = A, \quad (6)$$

where A is constant for a given nanomaterial.

In view of equation (6), equation (4) can be written as

$$\frac{dB}{B} = \left[\frac{-A}{V_o} + \frac{1}{V}\right] dV \quad (7)$$

Integrating eq. (7), we get

$$\frac{B}{B_o} = \frac{V}{V_o} \exp A\left[1 - \frac{V}{V_o}\right] \quad (8)$$

Where B_T is equal to

$$B = -V\left(\frac{dP}{dV}\right)_T \quad (9)$$

Now, using equation (8), equation (9) can be represented as

$$\frac{B}{B_o} \exp A\left[1 - \frac{V}{V_o}\right] dV = -dP \quad (10)$$

The integration of equation (10) gives

$$P = \frac{B_o}{A}\left[\exp A\left[1 - \frac{V}{V_o}\right] - 1\right] \quad (11)$$

Here B_o is the bulk modulus at zero pressure and the constant A is determined from the initial conditions, i.e. at $V = V_o$,

$$A = \delta_T^o + 1$$

On substitution of constant A in equation (11) and taking natural log, we get the following final form of usual Tait's equation of state,

$$V(P,T_o)/V(o,T_o) = 1 - \frac{1}{B_o'+1}\log\left[1 + \left\{\frac{B_o'+1}{B_o}\right\}P\right] \quad (12)$$

where $V(P,T_o)$ is the volume of the solid at pressure required to compress the unit cell ,keeping the temperature constant,V_o is the initial volume at P=0 at room temperature T_o. B_o and B'_o are the isothermal bulk modulus and its first pressure derivative at T= T_o. The beauty of above described this equation of state is that it requires only two input parameters B_o and B'_o at zero pressure value. As an application of this equation of state (as in bulk materials), we have employed Tait's equation of state to predict the transition pressure (P_T) in ZnO nanocrystal. It is pertinent to mention here that we have used the best fit experimental values of B_o and B'_o. in the present study. The above equation (12) provides a simple and straight forward approach to predict the relative compression in solids at high pressures.

3. RESULTS AND DISCUSSION

In the present investigation, we have presented a simple theory to predict the effect of pressure on ZnO nanocrystal and its counterpart bulk ZnO nanocrystal. The values of transition pressure have been calculated from the equation of state (12) and the results achieved in the present study are reported in figure 1 respectively along with the experimental data[12]. The two input parameters viz. B_o and B'_o used in equation of state are shown in table 1 along with the percentage of cell volume collapsed during transformation in ZnO nanostructure at the transition pressure. The values of transition pressure calculated from the Tait's equation of state is found in close agreement with the

experimental values. It can be seen from the Table 1 that the transition pressure in nano-ZnO increases as the volume compression decreases in comparison to its bulk ZnO during the transformation from hexagonal wurtzite (B4) phase to the cubic rock salt (B1) phase under pressure. This difference of transition pressure is attributed to micro strains the increment in surface-volume ratio depending on the nanomorphologies of the material. It may thus be concluded that the value of the transition pressure in nanomaterial depends on the compression behavior of unit cell volume during the transformation from wurtzite (B4) phase to the cubic rock salt (B1) phase under pressure.

The results obtained in the present study are found in good agreement with the experimental data, which demonstrate the validity of the formulation developed. The variation of bulk modulus with pressure for nano-ZnO is shown in figure 2.The values of bulk modulus calculated from equation (8) at different pressures, however, could not be compared with the experimental data because the data on them are not available so far. Our calculated results on bulk modulus properties of nano-ZnO may, however, stimulate the experimental investigation in future. It may thus be emphasized that the present investigation provides a simple method to study the effect of high pressure on nanostructured materials successfully. The high pressure study of nanomaterials is an appealing and highly expanding area of research for both applied sciences and nanotechnology.

Table1: Input data and the values of transition pressure (P_T) calculated in the present study

Crystal	Bulk modulus B_o (GPa) B4phase	Bulk modulus B_o (GPa) B1phase	B'_o B4 phase	B'_o B1 phase	Transition pressure P_T (GPa) calculated	P_T (GPa) Mixed phase (B4+B1) Expt.	Volume compression (calculated)	Volume compression (exp.)
ZnO–nanocrystal (50 nm)	151[20]	221[24]	4	4	10.5	10.5-13[12]	17.1%	17.5%[12]
ZnO–Bulkcrystal	154[23]	229[23]	4	4	9	8.9-11.5 [12]	19%	16.5%[15]

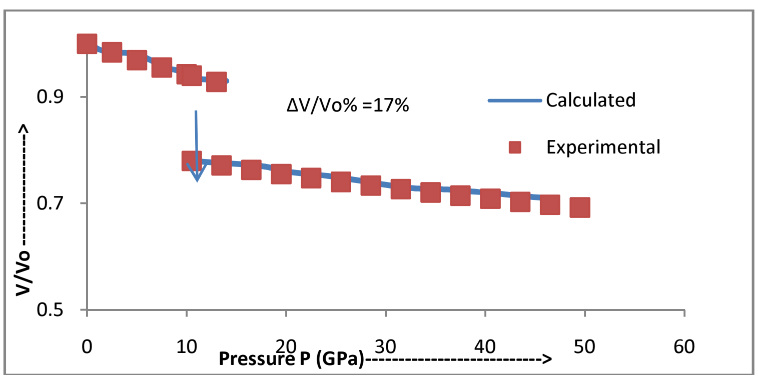

Figure 1:Variation of V/Vo vs P for ZnO nanocrystal

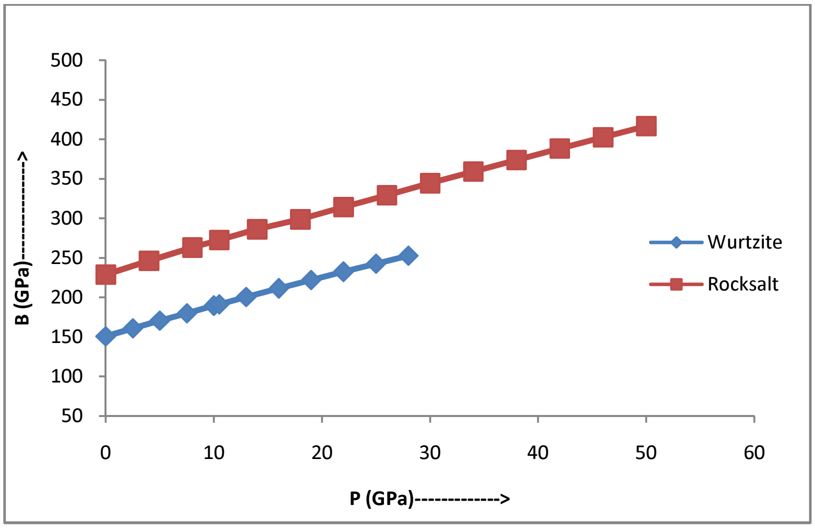

Figure 2: Variation of B vs P for ZnO nanocrystal

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